

Research Highlight

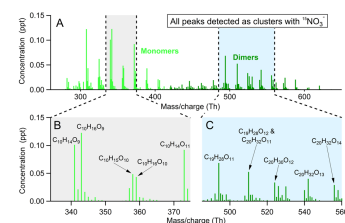
The growth of newly formed particles from sizes of less than three nanometers up to the sizes of cloud condensation nuclei (about one hundred nanometers) in many continental ecosystems require abundant, essentially non-volatile organic vapours. However, the sources and compositions of such vapors were previously unknown. This research found that ozonolysis of monoterpenes, a ubiquitous oxidation process, leads directly to the formation of extremely low-volatility vapors. These vapors were found to form at significant mass yield in the gas phase and condense irreversibly onto aerosol surfaces to produce secondary organic aerosols (SOAs), helping to explain both the discrepancy between observed and modeled SOA burdens and how these low-volatility vapors can enhance, or even dominate, the formation and growth of aerosol particles over forested regions. Thus, these results provide a missing link between biogenic volatile organic compounds (VOCs) and their conversion to aerosol particles.

The researchers used high-resolution chemical ionization mass spectrometers, a nitrate chemical ionization with the atmospheric pressure interface time-of-flight mass spectrometer (CI-API-TOF), and an iodide volatilization impactor (HRTof-CIMS). These detected a suite of semi-volatile and low volatility, highly oxygenated, high-molecular-mass gas-phase oxidation products from several precursors following both ozonolysis and reaction with the hydroxyl radical (OH) in the Julich Plant Atmosphere Chamber (JPAC). In particular, the nitrate CI-API-TOF monoterpene ozonolysis spectra displayed highly oxygenated monomer ($C_{10}H_{14}O_7$ [7–11]) and dimer ($C_{19-20}H_{28-32}O_{10-18}$) patterns of compounds that presumably have saturation vapor concentrations far lower than typically reported for gas-phase species measured in chamber experiments. With the experimental conditions probed in JPAC, both daytime and night-time mass spectra could be closely replicated with compounds recorded at a boreal forest site in Hyytiälä, Finland.

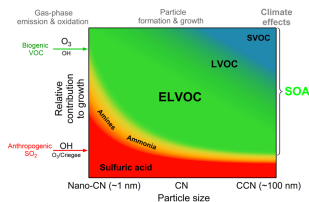
Extremely low volatility organic compounds (ELVOCs) formed at an estimated mole yield of 7 percent (+/- 3.5 percent), which implies a 15 percent mass yield due to the large molecular weights. This finding alone implies a lower limit to the SOA mass yield from monoterpene ozonolysis that will be independent of existing organic aerosol mass. That is because these ELVOCs irreversibly condensed onto chamber walls and solid ammonium sulfate seed to form SOA. In fact, the measured loss of ELVOC to the seed particles corresponded to 2/3 of the formed SOA from <1 up to 10 micrometers/ m^3 of SOA.

Consistent with their composition and condensation to seed particles, these ELVOCs were highly correlated with the number of particles > 3 nanometers in size, and the dimer ELVOCs were highly correlated with the number of particles < 1.5 nanometers in size, suggesting that the measured ELVOC can act as nano condensation nuclei and play a role in the earliest stages of new particle formation. Indeed, the concentrations of these ELVOC measured at a boreal forest field station were capable of explaining observed particle growth rates during new particle formation events.

This research provided the first molecular elucidation and quantification of a direct and ubiquitous source of ELVOCs produced in the gas phase from oxidation of monoterpenes and other VOCs. This source is capable of explaining nanoparticle growth in boreal regions, and a significant fraction of low-volatility SOAs are currently missing, or poorly described, in atmospheric models. Some atmospheric models can replicate monoterpene SOAs by assuming irreversible condensation of unspecified first-generation oxidation products. This is an approach now validated and clarified by these results. Also demonstrated were mechanisms whereby anthropogenic emissions (SO_2 , NO) can affect the contribution of biogenic VOCs to aerosol particle formation and growth by interacting with ELVOCs directly (for example, H_2SO_4) or altering their formation pathways (for example, NO).



High resolution online mass spectra from a-pinene ozonolysis showing the presence of highly oxygenated and high molecular weight compounds that exhibited behavior consistent with being extremely low volatility organic compounds (ELVOC).



A schematic showing the role of ELVOC in the formation and growth of new particles, and their contribution to SOA in a boreal forest region.

These results demonstrate current oxidation mechanisms underestimate the role of ozone and RO₂ isomerization chemistry in producing highly oxygenated low-volatility compounds. This underlines the importance of accurately predicting oxidant levels and biogenic VOC emissions. These new insights into ELVOC formation may help to more accurately quantify the effects of changes in biogenic VOC emissions, specifically, the effects on new particle formation, abundance of cloud condensation nuclei, and possible related climate feedbacks.

Reference(s)

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Working Group(s)

Aerosol Life Cycle